

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-041309
(43)Date of publication of application : 13.02.1996

(51)Int.CI. C08L 71/10
C08L 79/08
C23F 4/00
H01L 21/302

(21)Application number : 06-195911 (71)Applicant : HOECHST JAPAN LTD
(22)Date of filing : 28.07.1994 (72)Inventor : OSHITA TETSUYA

(54) POLYBENZIMIDAZOLE RESIN ARTICLE FOR DRY ETCHING APPARATUS

(57) Abstract:

PURPOSE: To prepare a resin article for a dry etching apparatus which can prevent deterioration, prolong the service life and rationalize the maintenance by using a mixture of polybenzimidazole with a polyarylene ketone to form at least the surface of the article.

CONSTITUTION: A resin article for use within or around a dry etching apparatus, wherein at least the surface of the article comprises an intimate mixture contg. 10 to 80wt.% polybenzimidazole and 90 to 20wt.% polyarylene ketone. The mixture has excellent heat, chemical and, radiation resistances and other properties and is very suited as a material for components used within or around a dry etching apparatus where heat and plasma resistances are required. The components include, for example, bolts, nuts, and bush bearing. Examples of members to be etched include semiconductor wafers, liquid crystal displays, and hard disks.

CLAIMS

[Claim(s)]

[Claim 1] Goods made of poly benzimidazole system resin for dry etching systems characterized by consisting of the homogeneity mixture with which it is the goods used on the outskirts of it within the chamber of a dry etching system, and a surface part contains 10 - 80 % of the weight of poly benzimidazoles, and 90 - 20 % of the weight of the poly arylene ketones at least.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the goods used for dry etching systems, such as an etching system as a semi-conductor processor, especially a plasma etching system.

[0002]

[Description of the Prior Art] In the process which manufactures the semi-conductor for electronics, in order to add impurities, such as Lynn, boron, and arsenic, from the front face of the silicon wafer used as a substrate, the oxide film of a desired part is removed or actuation which processes the metal membrane vapor-deposited on the front face, and makes an electrode and wiring is performed. Generally this actuation is called etching.

[0003] When it divides roughly, there are wet etching and dry etching in etching. Wet etching is the approach of dissolving with a chemical the ingredient which it is going to remove. For example, although a silicon dioxide is dissolved in a hydrofluoric acid, an oxidizing agent and the etching reagent which consists of a hydrofluoric acid can be used for removal of an oxide film using silicon hardly dissolving.

[0004] On the other hand, dry etching is the approach of etching by supplying gas to the silicon wafer which carried out pattern formation with lithography, making a reaction cause, and making the matter with high vapor pressure, or the volatile high matter generate. Dry etching is classified into plasma etching and reactive ion etching (RIE) according to technique. Since more detailed processing can do dry etching as compared with wet etching, the etching method has dry etching in use current [which the demand level over a fine ***** process develops increasingly with the flow of high integration of a semiconductor device, and advanced features].

[0005] Synthetic resin, the ceramics, or a quartz is used by the reasons of insulation, corrosion resistance, etc. as the quality of the material of goods, such as a bolt used into a dry etching system, and a nut. Especially, in the case of plasma etching, an operating condition is an elevated temperature, and since the plasma is also easy to be invaded, the high resin of thermal resistance, insulation, and plasma-proof nature, for example, polyimide, a fluororesin, a polycarbonate, aromatic polyester, etc. are used. Moreover, although the goods used around a dry etching system are also partial, since it is exposed to an etching environment, insulation and thermal resistance are required.

[0006] However, since the resin of thermal resistance, plasma-proof nature, or a mechanical strength, such as polyimide conventionally used for the dry etching system, was insufficient, when this resin was used as ingredients, such as a bolt of a dry etching system, a nut, a bush bearing, or a fixture for immobilization, by it, there were many problems, like the erosion [exhausting / by overheating] by the plasma, destruction by degradation on the strength, and PATIKURU contamination break out.

[0007] Moreover, the homogeneity mixture of the poly benzimidazole and the poly

arylene ketone and its sintered compact, and an injection-molded product are indicated by JP,3-41150,A and JP,2-29683,A, and a sintered compact and an injection-molded product are Hoechst further. Although marketed as Celazole (trademark) of Celanese, as for the application to various kinds of goods of a dry etching system, neither publication nor suggestion is carried out at all.

[0008]

[Problem(s) to be Solved by the Invention] This inventions are various goods used on the outskirts of it within the dry etching system which solved said conventional trouble, prevent the degradation and aim at offering the goods made of poly benzimidazole system resin for dry etching systems which can improve rationalization of the maintenance accompanying reinforcement, breakage, etc. as a result the reinforcement of the etching system itself, rationalization, and the engine performance.

[0009]

[Means for Solving the Problem] According to this invention, it is the goods used on the outskirts of it within the chamber of a dry etching system, and the goods made of poly benzimidazole system resin for dry etching systems characterized by consisting of the homogeneity mixture with which a surface part contains 10 - 80 % of the weight of poly benzimidazoles and 90 - 20 % of the weight of the poly arylene ketones at least are offered.

[0010] Hereafter, this invention is further explained to a detail. The poly benzimidazole (henceforth "PBI") used for the ingredient of the goods of this invention It is the heterocycle type polymer excellent in thermal stability, anti-oxidation resolvability, hydrolysis-proof nature, etc. For example, one sort or two sorts or more of aromatic series tetra-amines, One sort or two sorts or more of aromatic series, aliphatic series or heterocycle type dicarboxylic acid, its ester, or an anhydride It can manufacture by carrying out the melting polymerization of the one step with law or a two step method. The manufacture approach Many the United States patent No. 26,065, for example, U.S. reissue patent, United States patent 3,313,783rd, 3,509,108, 3,518,234, 3,555,389, 3,433,772, 3,408,336, 3,578,644, 3,549,603, 3,708,439, 4,154,919, 4,312,976, 4, 377, It is indicated by No. 546 or 4,549,388. Moreover, the manufacture approach of PBI is J.P.Critchley, G.J.Knight, and "thermal-resistance polymer written by W.W.Wright. - It is useful ingredient (Heat-Resistant Polymers-Technologically Useful Materials)"Plenum technically. Press, New It explains also to York (1983) and the 259-322nd page.

[0011] The condensation reaction of said aromatic series tetra-amine, and a said aromatic series, aliphatic series or heterocycle type dicarboxylic acid, its ester or an anhydride shows below the reaction formula which makes the poly benzimidazole generate.

[Table 1]

R is a tetravalent aromatic series radical among {type, and the joint hand with the amino group has become a pair, the contiguity carbon atom, i.e., the alt.carbon atom, of the nucleus. R' is the aromatic series radical, alkylene group, or heterocycle radical of bivalence. (In addition, R and R' may be one sort or two sorts or more of each radicals, respectively.)

Y expresses a hydrogen atom, an aryl group, and an alkyl group. }

[0012] The aromatic series tetra-amine component which can be used in this invention has for example, the following general formula (I).

[Formula 1]

(R is a thing as described above among a formula.)

[0013] As an example of an aromatic series tetra-amine component, what is shown in the following table 2 is mentioned.

[Table 2]

(X expresses a low-grade alkylene group like -O-, -S-, -SO₂- or -CH₂-, -(CH₂)₂-, or -C(CH₃)₂- among a formula.)

A desirable aromatic series tetra-amine is a 3, 3', 4, and 4'-tetra-amino biphenyl.

[0014] The dicarboxylic acid component (a free acid, ester, and an anhydride are included) which can be used in this invention has for example, the following formula. [Formula 2]

(Among a formula, although Y can be a hydrogen atom, an aryl group, or an alkyl group, 95% or less of Y is hydrogen or phenyl.)

Therefore, although a dicarboxylic acid component can consist of mixture [of mixture; diester and/or monoester with a free acid, at least one diester, and/or monoester]; or single dialkyl ester, monoester, mixed arylated alkyl or alkyl / alkyl ester, all can consist of a free acid or diphenyl ester. When Y is alkyl, Y is methyl most preferably including 1 thru/or five carbon atoms. the alkyl in which Y contains 1 thru/or five carbon atoms when Y is aryl, or alkoxy ** -- or [permuting by the radical of the inactive monovalence of arbitration / like] -- or it can be non-permuted said R or R'. It can be the aromatic series radical of the monovalence of the arbitration obtained by saturating all valences with hydrogen except for one of the aromatic series radicals. As an example of this aryl group, they are phenyl, naphthyl, three kinds of phenyl groups, and three kinds of tolyl groups. A desirable aryl group is usually phenyl.

[0015] There is heterocycle type dicarboxylic acid aromatic series dicarboxylic acid; aliphatic series dicarboxylic acid (what has 4 thru/or eight carbon atoms preferably);, and whose carboxyl group are substituents on the carbon atom in a pyridine, pyrazine, a furan, a quinoline, a thiophene, and a ring compound like a pyran among the dicarboxylic acid with the suitable dicarboxylic acid used in this invention.

[0016] The dicarboxylic acid which can be used as a free acid or ester as described above is aromatic series dicarboxylic acid as shown in the following table 3.

[Table 3]

(X is as having set in the aromatic series tetra-amine previously among a formula.)

[0017] For example, the following dicarboxylic acid can be used suitably. Namely, isophthalic acid; terephthalic-acid;4, 4'-biphenyl dicarboxylic acid;1, 4-naphthalene dicarboxylic acid; diphenic acid (2. and 2'-biphenyl dicarboxylic acid); phenyl indan dicarboxylic acid;1, 6-naphthalene dicarboxylic acid;2, 6-naphthalene dicarboxylic acid;4, and 4'-diphenyl ether dicarboxylic acid; 4 and 4'-diphenyl thioether dicarboxylic acid. It is the dicarboxylic acid most desirable [among these] although isophthalic acid uses for the approach of this invention as a free acid or ester.

[0018] A dicarboxylic acid component can be used at a rate of about one mol of the total dicarboxylic acid components per one mol of aromatic series tetra-amines.

However, it can ask for the optimal ratio of the reactant in a specific polymerization system easily by this usual contractor.

[0019] There are the following in the example of the poly benzimidazoles which can be prepared by the above approaches. that is Polly 2, 2'- (m-phenylene)-5 and 5'-bibenzimidazol; Polly 2, 2' - (biphenylene-2", 2"-5, 5'-bibenzimidazol; Polly 2, 2'-(biphenylene - 4", 4")-5, and 5'-bibenzimidazol;) [Polly 2,] [2'-] (1", 1", and 3"-trimethyl in DANIREN)-3" and 5"-p-phenylene -5, 5'-bibenzimidazol; 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol / 2, and 2- (1" and 1" --) 3"-trimethyl in DANIREN - 5" and 3"- (p-phenylene)-5, 5'-bibenzimidazol copolymer; 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol-2", 2", 5, and 5'-bibenzimidazol copolymer; Polly 2, 2'-(FURIREN - 2", 5")-5, 5'-bibenzimidazol; Polly 2, 2'-(Naphthalene-1", 6")-5, 5'-bibenzimidazol; Polly 2, 2'-(naphthalene - 2", 6")-5, 5'-bibenzimidazol; Polly 2, the 2'-amylene -5, 5'-bibenzimidazol; Polly 2, the 2'-octamethylene -5, 5'-bibenzimidazol; Polly 2, 2'- 2'-(m-phenylene)-G MIDAZO benzene; -- Polly 2, 2'-cyclohexenyl -5, 5'-bibenzimidazol; Polly 2, 2'-(m-phenylene)-5, and 5'-JI (benzimidazole) ether; Polly 2 -- (m-phenylene) -5, 5'-JI Sulfide; Polly 2, 2'-(Benzimidazole) (m-phenylene) -5, 5'-JI Sulfone; Polly 2, 2'-(Benzimidazole) (m-phenylene) -5, 5'-JI Methane; (Benzimidazole) Polly 2, 2"--(m-phenylene)-5, and 5"-JI (benzimidazole) propane -2, 2; polyethylene -1, 2-2, 2"--(m-phenylene)-5, and 5"-JI (benzimidazole) ethylene - 1 Two (in this case) The double bond of ethylene remains into the last polymer. As a desirable polymer, it is Polly 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol.

[0020] The poly arylene ketone used in this invention is excellent in chemical resistance etc., for example, is expressed with the following general formula.

[Formula 3]

It is expressed with (the inside of a formula, and X, Y and n are integers). The typical poly arylene ketone is shown below. The following repeat unit: [Formula 4]

The polyether ketone which ****. The following repeat unit: [Formula 5]

The polyether ether ketone which **** (PEEK). This polyether ether ketone is crystalline thermoplastics which has a property similar to polyether ketones. The following repeat unit: [Formula 6]

The polyether ether ketone ketone which ****. The following repeat unit: [Formula 7]

The polyether ketone ketone which ****. The poly arylene ketone useful to operation of this invention is a polyether ketone or a polyether ether ketone.

[0021] Generally, the poly benzimidazole has good chemical resistance and big compressive strength, and holds those properties also in an elevated temperature. On the other hand, although the poly arylene ketones have the compressive strength of whenever [good chemical resistance and middle], as compared with the poly benzimidazole, a hot mechanical property is inferior. As mentioned above, for a working limit, to an application being restricted, since [heat-resistant and pressure-

resistant] the mold goods of the poly arylene ketones are inadequate, as for the mold goods of the poly benzimidazole, an application is restrained.

[0022] In this invention, the mold goods which have the thermal resistance, the chemical resistance, and the strength property which were excellent by using the homogeneity mixture of the poly benzimidazole and the poly arylene ketone can be manufactured. The blending ratio of coal of this mixture is 10 - 80 % of the weight of poly benzimidazoles, and 90 - 20 % of the weight of the poly arylene ketones.

[0023] The mixture of PBI preferably used for the ingredient of the goods of this invention is mixture with the polyether ether ketone shown with Polly [who is shown with the following structure expression (VIII)] 2, 2'-(m-phenylene)-5, and 5'-bibenzoimidazol, and the following structure expression (IX).

[Formula 8]

(n shows polymerization degree among a formula.)

[Formula 9]

(m shows polymerization degree among a formula.)

[0024] The PBI homogeneity mixture used in this invention is excellent in thermal resistance, chemical resistance, radiation resistance, etc., and very suitable as the quality of the material of the components used on the outskirts of it within the dry etching system with which thermal resistance and plasma-proof nature are demanded.

[0025] There are goods which the goods widely used on the outskirts of it within the chamber of a dry etching system are included, for example, are similar to a bolt, a nut, a bush bearing, a clamp ring or the fixture for etched member immobilization, and them among the goods to which PBI mixture is given in this invention. An etched member means the thing of a member which receives etching processing by dry etching, for example, has a semi-conductor wafer, a liquid crystal display panel, a hard disk, etc.

[0026] Moreover, in this invention, in the chamber of a dry etching system, the reaction place exposed to an etching environment is said, and the components with which the circumference fixes wrap quartz components for a chamber and this chamber from the exterior are said.

[0027] In this invention, the equipment which etches is said by supplying gas to the silicon wafer which carried out pattern formation with lithography, as described above as the dry etching system, making a reaction cause, and making the matter with high vapor pressure, or the volatile high matter generate. Preferably, the dry etching system with which the components of this invention are used is a plasma etching system.

[0028] There is especially no limit in the production approach of the goods which consist of the PBI mixture by this invention. For example, sinter molding is carried out to the configuration of a request of the powder of PBI mixture, or PBI mixture is pelletized, and it casts in a desired configuration by the injection-molding approach. For example, the shaping approach of this seed PBI mixture is indicated by said JP,3-41150,A and JP,2-296834,A, and can be fabricated by the same approach.

[0029] In this invention, PI, PAI, the glass fiber, aluminum 2O3, and the carbon fiber other than PBI and the poly arylene ketone may be mixed.

[0030]

[Example] Hereafter, based on an example and the example of a comparison, this invention is further explained to a detail.

[An example 1], the [example 1 of a comparison]

About the clamp ring for 5 inch silicon wafers, and the fixture for immobilization, it is the Toyo Machinery & Metals Co., Ltd. make. Injection molding was carried out using the injection molding machine. The ingredient of a fixture shows the following.

** PBI/PEEK is the mixture of 50 % of the weight of polyether ether ketones shown by 50 % of the weight of Polly 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol, and said formula (IV).

** The polycarbonate shown by the polyether ether ketone ** polycarbonate following-ization 10 shown by the PBI Polly 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol ** PEEK aforementioned formula (IV) [** 10]

(n shows polymerization degree among a formula.)

** Aromatic polyester shown by the aromatic polyester following-ization 11 [** 11]

(n shows polymerization degree among a formula.)

** Polyimide shown by the polyimide following-ization 12 [** 12]

(n shows polymerization degree among a formula.)

[0031] This fixture for immobilization was mounted in the plasma etching system, etching actuation was performed, and the good use life was compared. Dirt [exhausting / a crack and] etc. produced the good use life in this fixture, and exchange or washing distinguished visually whether it was the need. The result is shown in Table 4 as a life of an ingredient. Moreover, the result of having measured the amount of particle of these rings with the particle counter is shown in Table 4. Under the present circumstances, the amount of particle of a polycarbonate was set to 100.

[0032]

[Table 4]

[0033] [Example 2] Engine-lathe processing of the compression-molding object of PBI (poly benzimidazole used in the example 1) / PEEK mixture (40wt%:60wt%) was carried out, and the metric coarse thread of M6 was produced. The chamber of a plasma etching system and it were used for immobilization with a wrap quartz tube for this screw, and chemical resistance, abrasion resistance, and mechanical strength degradation were observed. The chemical used within the chamber was tetrafluoromethane. Consequently, even if three months passed after use, it was changeless to the physical properties of a screw.

[0034] [Example 2 of a comparison] The screw which has the same dimension as an example 2 was produced by being made from a polycarbonate. This screw was used for the same part as an example 2, and chemical resistance, abrasion resistance, and mechanical strength degradation were observed under the same conditions as an example 2. Consequently, after use, in four weeks, a remarkable change of a crack, wear, etc. arose and it became use impossible.

[0035]

[Effect of the Invention] Like this invention, by using the homogeneity mixture containing PBI and the poly arylene ketone as an ingredient of the goods used on the

outskirts of it within the chamber of a dry etching system, degradation by the plasma of these goods etc. was prevented and rationalization of the maintenance accompanying reinforcement, breakage, etc. as a result the reinforcement of the etching system itself, rationalization, and an engine-performance improvement were attained.

TECHNICAL FIELD

[Industrial Application] This invention relates to the goods used for dry etching systems, such as an etching system as a semi-conductor processor, especially a plasma etching system.

PRIOR ART

[Description of the Prior Art] In the process which manufactures the semi-conductor for electronics, in order to add impurities, such as Lynn, boron, and arsenic, from the front face of the silicon wafer used as a substrate, the oxide film of a desired part is removed or actuation which processes the metal membrane vapor-deposited on the front face, and makes an electrode and wiring is performed. Generally this actuation is called etching.

[0003] When it divides roughly, there are wet etching and dry etching in etching. Wet etching is the approach of dissolving with a chemical the ingredient which it is going to remove. For example, although a silicon dioxide is dissolved in a hydrofluoric acid, an oxidizing agent and the etching reagent which consists of a hydrofluoric acid can be used for removal of an oxide film using silicon hardly dissolving.

[0004] On the other hand, dry etching is the approach of etching by supplying gas to the silicon wafer which carried out pattern formation with lithography, making a reaction cause, and making the matter with high vapor pressure, or the volatile high matter generate. Dry etching is classified into plasma etching and reactive ion etching (RIE) according to technique. Since more detailed processing can do dry etching as compared with wet etching, the etching method has dry etching in use current [which the demand level over a fine ***** process develops increasingly with the flow of high integration of a semiconductor device, and advanced features].

[0005] Synthetic resin, the ceramics, or a quartz is used by the reasons of insulation, corrosion resistance, etc. as the quality of the material of goods, such as a bolt used into a dry etching system, and a nut. Especially, in the case of plasma etching, an operating condition is an elevated temperature, and since the plasma is also easy to be invaded, the high resin of thermal resistance, insulation, and plasma-proof nature, for example, polyimide, a fluororesin, a polycarbonate, aromatic polyester, etc. are used. Moreover, although the goods used around a dry etching system are also partial, since it is exposed to an etching environment, insulation and thermal resistance are required.

[0006] However, since the resin of thermal resistance, plasma-proof nature, or a mechanical strength, such as polyimide conventionally used for the dry etching system, was insufficient, when this resin was used as ingredients, such as a bolt of a dry etching system, a nut, a bush bearing, or a fixture for immobilization, by it, there were many problems, like the erosion [exhausting / by overheating] by the plasma, destruction by degradation on the strength, and PATIKURU contamination break out.

[0007] Moreover, the homogeneity mixture of the poly benzimidazole and the poly

arylene ketone and its sintered compact, and an injection-molded product are indicated by JP,3-41150,A and JP,2-29683,A, and a sintered compact and an injection-molded product are Hoechst further. Although marketed as Celazole (trademark) of Celanese, as for the application to various kinds of goods of a dry etching system, neither publication nor suggestion is carried out at all.

EFFECT OF THE INVENTION

[Effect of the Invention] Like this invention, by using the homogeneity mixture containing PBI and the poly arylene ketone as an ingredient of the goods used on the outskirts of it within the chamber of a dry etching system, degradation by the plasma of these goods etc. was prevented and rationalization of the maintenance accompanying reinforcement, breakage, etc. as a result the reinforcement of the etching system itself, rationalization, and an engine-performance improvement were attained.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This inventions are various goods used on the outskirts of it within the dry etching system which solved said conventional trouble, prevent the degradation and aim at offering the goods made of poly benzimidazole system resin for dry etching systems which can improve rationalization of the maintenance accompanying reinforcement, breakage, etc. as a result the reinforcement of the etching system itself, rationalization, and the engine performance.

MEANS

[Means for Solving the Problem] According to this invention, it is the goods used on the outskirts of it within the chamber of a dry etching system, and the goods made of poly benzimidazole system resin for dry etching systems characterized by consisting of the homogeneity mixture with which a surface part contains 10 - 80 % of the weight of poly benzimidazoles and 90 - 20 % of the weight of the poly arylene ketones at least are offered.

[0010] Hereafter, this invention is further explained to a detail. The poly benzimidazole (henceforth "PBI") used for the ingredient of the goods of this invention It is the heterocycle type polymer excellent in thermal stability, anti-oxidation resolvability, hydrolysis-proof nature, etc. For example, one sort or two sorts or more of aromatic series tetra-amines, One sort or two sorts or more of aromatic series, aliphatic series or heterocycle type dicarboxylic acid, its ester, or an anhydride It can manufacture by carrying out the melting polymerization of the one step with law or a two step method. The manufacture approach Many the United States patent No. 26,065, for example, U.S. reissue patent, United States patent 3,313,783rd, 3,509,108, 3,518,234, 3,555,389, 3,433,772, 3,408,336, 3,578,644, 3,549,603, 3,708,439, 4,154,919, 4,312,976, 4, 377, It is indicated by No. 546 or 4,549,388. Moreover, the manufacture approach of PBI is J.P.Critchley, G.J.Knight, and "thermal-resistance polymer written by W.W.Wright. - It is useful ingredient (Heat-Resistant Polymers-Technologically Useful Materials)"Plenum technically.

Press, New It explains also to York (1983) and the 259-322nd page.

[0011] The condensation reaction of said aromatic series tetra-amine, and a said aromatic series, aliphatic series or heterocycle type dicarboxylic acid, its ester or an anhydride shows below the reaction formula which makes the poly benzimidazole generate.

[Table 1]

R is a tetravalent aromatic series radical among {type, and the joint hand with the amino group has become a pair, the contiguity carbon atom, i.e., the alt.carbon atom, of the nucleus. R' is the aromatic series radical, alkylene group, or heterocycle radical of bivalence. (In addition, R and R' may be one sort or two sorts or more of each radicals, respectively.)

Y expresses a hydrogen atom, an aryl group, and an alkyl group. }

[0012] The aromatic series tetra-amine component which can be used in this invention has for example, the following general formula (I).

[Formula 1]

(R is a thing as described above among a formula.)

[0013] As an example of an aromatic series tetra-amine component, what is shown in the following table 2 is mentioned.

[Table 2]

(X expresses a low-grade alkylene group like -O-, -S-, -SO₂- or -CH₂-, -(CH₂)₂-, or -C(CH₃)₂- among a formula.)

A desirable aromatic series tetra-amine is a 3, 3', 4, and 4'-tetra-amino biphenyl.

[0014] The dicarboxylic acid component (a free acid, ester, and an anhydride are included) which can be used in this invention has for example, the following formula.

[Formula 2]

(Among a formula, although Y can be a hydrogen atom, an aryl group, or an alkyl group, 95% or less of Y is hydrogen or phenyl.)

Therefore, although a dicarboxylic acid component can consist of mixture [of mixture; diester and/or monoester with a free acid, at least one diester, and/or monoester]; or single dialkyl ester, monoester, mixed arylated alkyl or alkyl / alkyl ester, all can consist of a free acid or diphenyl ester. When Y is alkyl, Y is methyl most preferably including 1 thru/or five carbon atoms. the alkyl in which Y contains 1 thru/or five carbon atoms when Y is aryl, or alkoxy ** -- or [permuting by the radical of the inactive monovalence of arbitration / like] -- or it can be non-permuted said R or R'. It can be the aromatic series radical of the monovalence of the arbitration obtained by saturating all valences with hydrogen except for one of the aromatic series radicals. As an example of this aryl group, they are phenyl, naphthyl, three kinds of phenyl groups, and three kinds of tolyl groups. A desirable aryl group is usually phenyl.

[0015] There is heterocycle type dicarboxylic acid aromatic series dicarboxylic acid; aliphatic series dicarboxylic acid (what has 4 thru/or eight carbon atoms preferably);, and whose carboxyl group are substituents on the carbon atom in a pyridine, pyrazine,

a furan, a quinoline, a thiophene, and a ring compound like a pyran among the dicarboxylic acid with the suitable dicarboxylic acid used in this invention.

[0016] The dicarboxylic acid which can be used as a free acid or ester as described above is aromatic series dicarboxylic acid as shown in the following table 3.

[Table 3]

(X is as having set in the aromatic series tetra-amine previously among a formula.)

[0017] For example, the following dicarboxylic acid can be used suitably. Namely, isophthalic acid; terephthalic-acid; 4, 4'-biphenyl dicarboxylic acid; 1, 4-naphthalene dicarboxylic acid; diphenic acid (2 and 2'-biphenyl dicarboxylic acid); phenyl indan dicarboxylic acid; 1, 6-naphthalene dicarboxylic acid; 2, 6-naphthalene dicarboxylic acid; 4, and 4'-diphenyl ether dicarboxylic acid; 4 and 4'-diphenyl thioether dicarboxylic acid. It is the dicarboxylic acid most desirable [among these] although isophthalic acid uses for the approach of this invention as a free acid or ester.

[0018] A dicarboxylic acid component can be used at a rate of about one mol of the total dicarboxylic acid components per one mol of aromatic series tetra-amines.

However, it can ask for the optimal ratio of the reactant in a specific polymerization system easily by this usual contractor.

[0019] There are the following in the example of the poly benzimidazoles which can be prepared by the above approaches. that is Polly 2, 2'-(m-phenylene)-5 and 5'-bibenzoimidazol; Polly 2, 2' - (biphenylene-2", 2""-5, 5'-bibenzoimidazol; Polly 2, 2'-(biphenylene - 4", 4"")-5, and 5'-bibenzoimidazol;) [Polly 2,] [2'-] (1", 1", and 3"-trimethyl in DANIREN)-3" and 5"-p-phenylene -5, 5'-bibenzoimidazol; 2, 2'-(m-phenylene)-5, and 5'-bibenzoimidazol / 2, and 2- (1" and 1" --) 3"-trimethyl in DANIREN - 5" and 3"- (p-phenylene)-5, 5'-bibenzoimidazol copolymer; 2, 2'-(m-phenylene)-5, and 5'-bibenzoimidazol-2", 2", 5, and 5'-bibenzoimidazol copolymer; Polly 2, 2'-(FURIREN - 2", 5")-5, 5'-bibenzoimidazol; Polly 2, 2'-(Naphthalene-1", 6")-5, 5'-bibenzoimidazol; Polly 2, 2'-(naphthalene - 2", 6")-5, 5'-bibenzoimidazol; Polly 2, the 2'-amylene -5, 5'-bibenzoimidazol; Polly 2, 2'-octamethylene -5, 5'-bibenzoimidazol; Polly 2, 2'- 2'-(m-phenylene)-G MIDAZO benzene; -- Polly 2, 2'-cyclohexenyl -5, 5'-bibenzoimidazol; Polly 2, 2'-(m-phenylene)-5, and 5'-JI (benzimidazole) ether; Polly 2 -- (m-phenylene) -5, 5'-JI Sulfide; Polly 2, 2'-(Benzimidazole) (m-phenylene) -5, 5'-JI Sulfone; Polly 2, 2'-(Benzimidazole) (m-phenylene) -5, 5'-JI Methane; (Benzimidazole) Polly 2, 2'-(m-phenylene)-5, and 5"-JI (benzimidazole) propane -2, 2; polyethylene -1, 2-2, 2"--(m-phenylene)-5, and 5"-JI (benzimidazole) ethylene - 1 Two (in this case) The double bond of ethylene remains into the last polymer. As a desirable polymer, it is Polly 2, 2'-(m-phenylene)-5, and 5'-bibenzoimidazol.

[0020] The poly arylene ketone used in this invention is excellent in chemical resistance etc., for example, is expressed with the following general formula.

[Formula 3]

It is expressed with (the inside of a formula, and X, Y and n are integers). The typical poly arylene ketone is shown below. The following repeat unit: [Formula 4]

The polyether ketone which ****. The following repeat unit: [Formula 5]

The polyether ether ketone which **** (PEEK). This polyether ether ketone is crystalline thermoplastics which has a property similar to polyether ketones. The following repeat unit: [Formula 6]

The polyether ether ketone ketone which ****. The following repeat unit: [Formula 7]

The polyether ketone ketone which ****. The poly arylene ketone useful to operation of this invention is a polyether ketone or a polyether ether ketone.

[0021] Generally, the poly benzimidazole has good chemical resistance and big compressive strength, and holds those properties also in an elevated temperature. On the other hand, although the poly arylene ketones have the compressive strength of whenever [good chemical resistance and middle], as compared with the poly benzimidazole, a hot mechanical property is inferior. As mentioned above, for a working limit, to an application being restricted, since [heat-resistant and pressure-resistant] the mold goods of the poly arylene ketones are inadequate, as for the mold goods of the poly benzimidazole, an application is restrained.

[0022] In this invention, the mold goods which have the thermal resistance, the chemical resistance, and the strength property which were excellent by using the homogeneity mixture of the poly benzimidazole and the poly arylene ketone can be manufactured. The blending ratio of coal of this mixture is 10 - 80 % of the weight of poly benzimidazoles, and 90 - 20 % of the weight of the poly arylene ketones.

[0023] The mixture of PBI preferably used for the ingredient of the goods of this invention is mixture with the polyether ether ketone shown with Polly [who is shown with the following structure expression (VIII)] 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol, and the following structure expression (IX).

[Formula 8]

(n shows polymerization degree among a formula.)

[Formula 9]

(m shows polymerization degree among a formula.)

[0024] The PBI homogeneity mixture used in this invention is excellent in thermal resistance, chemical resistance, radiation resistance, etc., and very suitable as the quality of the material of the components used on the outskirts of it within the dry etching system with which thermal resistance and plasma-proof nature are demanded.

[0025] There are goods which the goods widely used on the outskirts of it within the chamber of a dry etching system are included, for example, are similar to a bolt, a nut, a bush bearing, a clamp ring or the fixture for etched member immobilization, and them among the goods to which PBI mixture is given in this invention. An etched member means the thing of a member which receives etching processing by dry etching, for example, has a semi-conductor wafer, a liquid crystal display panel, a hard disk, etc.

[0026] Moreover, in this invention, in the chamber of a dry etching system, the reaction place exposed to an etching environment is said, and the components with which the circumference fixes wrap quartz components for a chamber and this

chamber from the exterior are said.

[0027] In this invention, the equipment which etches is said by supplying gas to the silicon wafer which carried out pattern formation with lithography, as described above as the dry etching system, making a reaction cause, and making the matter with high vapor pressure, or the volatile high matter generate. Preferably, the dry etching system with which the components of this invention are used is a plasma etching system.

[0028] There is especially no limit in the production approach of the goods which consist of the PBI mixture by this invention. For example, sinter molding is carried out to the configuration of a request of the powder of PBI mixture, or PBI mixture is pelletized, and it casts in a desired configuration by the injection-molding approach. For example, the shaping approach of this seed PBI mixture is indicated by said JP,3-41150,A and JP,2-296834,A, and can be fabricated by the same approach.

[0029] In this invention, PI, PAI, the glass fiber, aluminum 2O₃, and the carbon fiber other than PBI and the poly arylene ketone may be mixed.

EXAMPLE

[Example] Hereafter, based on an example and the example of a comparison, this invention is further explained to a detail.

[An example 1], the [example 1 of a comparison]

About the clamp ring for 5 inch silicon wafers, and the fixture for immobilization, it is the Toyo Machinery & Metals Co., Ltd. make. Injection molding was carried out using the injection molding machine. The ingredient of a fixture shows the following.

** PBI/PEEK is the mixture of 50 % of the weight of polyether ether ketones shown by 50 % of the weight of Polly 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol, and said formula (IV).

** The polycarbonate shown by the polyether ether ketone ** polycarbonate following-ization 10 shown by the PBI Polly 2, 2'-(m-phenylene)-5, and 5'-bibenzimidazol ** PEEK aforementioned formula (IV) [** 10]

(n shows polymerization degree among a formula.)

** Aromatic polyester shown by the aromatic polyester following-ization 11 [** 11]

(n shows polymerization degree among a formula.)

** Polyimide shown by the polyimide following-ization 12 [** 12]

(n shows polymerization degree among a formula.)

[0031] This fixture for immobilization was mounted in the plasma etching system, etching actuation was performed, and the good use life was compared. Dirt [exhausting / a crack and] etc. produced the good use life in this fixture, and exchange or washing distinguished visually whether it was the need. The result is shown in Table 4 as a life of an ingredient. Moreover, the result of having measured the amount of particle of these rings with the particle counter is shown in Table 4. Under the present circumstances, the amount of particle of a polycarbonate was set to 100.

[0032]

[Table 4]

[0033] [Example 2] Engine-lathe processing of the compression-molding object of PBI (poly benzimidazole used in the example 1) / PEEK mixture (40wt%:60wt%) was carried out, and the metric coarse thread of M6 was produced. The chamber of a plasma etching system and it were used for immobilization with a wrap quartz tube for this screw, and chemical resistance, abrasion resistance, and mechanical strength degradation were observed. The chemical used within the chamber was tetrafluoromethane. Consequently, even if three months passed after use, it was changeless to the physical properties of a screw.

[0034] [Example 2 of a comparison] The screw which has the same dimension as an example 2 was produced by being made from a polycarbonate. This screw was used for the same part as an example 2, and chemical resistance, abrasion resistance, and mechanical strength degradation were observed under the same conditions as an example 2. Consequently, after use, in four weeks, a remarkable change of a crack, wear, etc. arose and it became use impossible.